

1007 Rec'd PCT/PTO 07 JAN 2002

Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (Rev. 5-93) TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NO H 3170 PCT/US U S APPLICATION NO (if known sec 17 CFR 1.5) <div style="font-size: 1.5em; font-weight: bold;">10/031740</div>
INTERNATIONAL APPLICATION NO. PCT/EP00/06159	INTERNATIONAL FILING DATE July 1, 2000	PRIORITY DATE CLAIMED July 6, 1999
TITLE OF INVENTION NOVEL DYES AND COLORANTS		
APPLICANT(S) FOR DO/EO/US Detlef Hollenberg, Horst Hoeffkes, Joachim-Kurt Foitzik, David Rose, Frank Naumann, and Leszek Wolfram		
Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information.		
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U S C 371. 2. <input type="checkbox"/> This a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S. C. 371(c)(2)). <ol style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S C. 371(c)(2)) 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U S C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S C 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C 371(c)(4)). UNEXECUTED 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C 371(c)(5)). 		
Items 11. to 16. below concern other document(s) or information included:		
<ol style="list-style-type: none"> 11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information. 		
Version with Markings to Show Changes Made; Information Disclosure Citation (Form PTO-1449) and References; and International Search Report		
"Express Mail" mailing label number EL615775445US		

U.S. Application No. (If known see CFR1.30) <div style="font-size: 1.5em; font-weight: bold;">10/031740</div>		INTERNATIONAL APPLICATION NO. PCT/EP00/06159		ATTORNEY'S DOCKET NUMBER H 3170 PCT/US	
17. ■ The following fees are submitted: Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO.....\$890.00 International preliminary examination fee paid to USPTO (37CFR 1.482)\$710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)). ..\$740.00 Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1 445(a)(2)) paid to USPTO. \$1,040.00 International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).. \$100.00				<div style="text-align: center;"> CALCULATIONS PTO USE ONLY </div>	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	890 00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				\$	
Claims	Number filed	Number Extra	Rate		
Total Claims	1- 20 =1	0	X 18.00	\$	0
Independent Claims	1- 3 =1	0	X 84.00	\$	00
Multiple dependent claims (s)(if applicable) 0			+ 280.00	\$	00
TOTAL OF ABOVE CALCULATIONS =				\$	890 00
Reduction by ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$	00
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1 492(f))...... +				\$	
TOTAL NATIONAL FEE =				\$	00
Fee for recording the enclosed assignment (37 CFR 1 21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$	890
				Amount to be refunded	\$-----
				charged	
<p>a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.</p> <p>b. ■ Please charge my Deposit Account No. <u>01-1250</u> in the amount of \$ 890.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. <u>02-0011</u>.</p> <p>c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u>. A triplicate copy of this sheet is enclosed</p> <p>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</p> <div style="display: flex; justify-content: space-between; margin-top: 20px;"> <div style="width: 60%;"> <p>SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Ste. 200 Gulph Mills, PA 19406.....</p> </div> <div style="width: 35%; text-align: center;"> <div style="font-size: 1.2em; font-family: cursive;">Kimberly R. Hild</div> <p>SIGNATURE</p> <hr style="border: 0; border-top: 1px solid black; margin: 5px 0;"/> <p>Kimberly R. Hild NAME ATTORNEY FOR APPLICANT 39,224 REGISTRATION NUMBER</p> </div> </div>					

10/031740

JC13 Rec'd PCT/PTO 07 JAN 2002

PATENT
Docket No. H 3170 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Hollenberg, et al.

International Application No. PCT/EP00/06159
International Filing Date: July 1, 2000

Serial No. To be assigned **Examiner:** To be assigned

Filed: To be assigned **Art Unit:** To be assigned

Title: NOVEL DYES AND COLORANTS

"Express Mail Post Office to Addressee" service mailing label number EL615775445US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

**Docket No. H3170 PCT/US
PCT/EP00/06159**

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP00/06159 filed on July 1, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 30 927.2 filed on July 6, 1999.

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

-- BACKGROUND OF THE INVENTION -- .

On page 3, on a separate line between lines 3 and 4, please insert the following header:

--SUMMARY OF THE INVENTION--.

On page 3, on a separate line between lines 19 and 20, please insert the following header:

-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 50, line 1, please delete the heading "CLAIMS" and insert therefor:

-- What is claimed is: --

On a separate page, after page 51, please insert the enclosed Abstract of the Disclosure.

In the Claims

Please cancel Claims 2 to 12, without prejudice.

**Docket No. H3170 PCT/US
PCT/EP00/06159**

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claim 1 will be pending after entry of the present amendment. Claims 2 to 12 are being canceled without prejudice.

Amendment

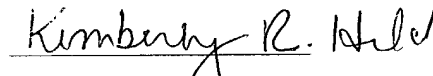
The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein. Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made." No new matter is added.

Docket No. H3170 PCT/US
PCT/EP00/06159

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,



Kimberly R. Hild
(Reg. No. 39,224)
Attorney for Applicants
(610) 278-4964

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

Rec'd PCT/PTO 18 JUN 2002 #4
10/031740

PATENT
Docket No. H 3170 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Hollenberg, et al.

International Application No. PCT/EP00/06159
International Filing Date: July 1, 2000

Serial No. 10/031,740 **Examiner:** To be assigned

Filed: To be assigned **Art Unit:** To be assigned
Confirmation No.: 8626

Title: NOVEL DYES AND COLORANTS

"Express Mail Post Office to Addressee" service mailing label number EV105943582 US

SUPPLEMENTAL PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Claims

Please cancel Claim 1 without prejudice.

Please add the following new claims:

Docket No. H3170 PCT/US
Serial No. 10/031,740
Confirmation No. 8626

-- 13. (NEW) A composition for coloring keratin fibers comprising a hybrid dye corresponding to formula (I):



wherein X is a group derived from a substantive dye;

wherein Y is a group derived from (i) a primary intermediate oxidation dye precursor, (ii) a secondary intermediate oxidation dye precursor, or (iii) a precursor of melanin that is a derivative of an indole or an indoline; and

wherein S is a direct bond or a spacer group.

14. (NEW) The composition of claim 13 further comprising at least one primary intermediate oxidation dye precursor or secondary intermediate oxidation dye precursor, or combinations thereof.

15. (NEW) The composition of claim 13 further comprising a substantive dye.

16. (NEW) The composition of claim 13 further comprising a precursor of melanin that is a derivative of an indole or a derivative of an indoline, or combinations thereof.

17. (NEW) The composition of claim 13 further comprising at least one compound selected from a primary intermediate oxidation dye precursor, a secondary intermediate oxidation dye precursor, a substantive dye, or a precursor of melanin that is a derivative of an indole or a derivative of an indoline; or combinations thereof.

Docket No. H3170 PCT/US
Serial No. 10/031,740
Confirmation No. 8626

18. (NEW) The composition of claim 17 further comprising at least one additive selected from a surfactant, a cationic polymer, an amphopolymer, an anionic polymer, or a nonionic polymer; or combinations thereof.

19. (NEW) The composition of claim 13 further comprising a surfactant.

20. (NEW) The composition of claim 19, wherein the surfactant comprises an anionic surfactant.

21. (NEW) The composition of claim 13 further comprising at least one cationic polymer or an amphopolymer, or combinations thereof.

22. (NEW) The composition of claim 13 further comprising at least one anionic polymer or nonionic polymer, or combinations thereof.

23. (NEW) The composition of claim 13 wherein X is derived from an azo dye, 3-nitroaniline, 2-amino-4-nitroaniline, 2-nitro-1,4-diaminobenzene, a derivative of 2-nitro-1,4-diaminobenzene, a derivative of 4-nitro-2-aminophenol, a derivative of 2-nitro-4-aminophenol, a derivative of 2-nitroaniline, a derivative of quinoxaline, a derivative of anthraquinone, or a derivative of naphthoquinone.

24. (NEW) The composition of claim 23 wherein Y is derived from p-phenylenediamine, p-aminophenol, 3,5-dimethoxybenzene, 1-naphthylamine, or 5,6-dimethoxyindoline.

25. (NEW) The composition of claim 24 wherein S is a direct bond or an alkylene group having 1 to 8 carbon atoms.

Docket No. H3170 PCT/US

Serial No. 10/031,740

Confirmation No. 8626

26. (NEW) The composition of claim 13 wherein Y is derived from 3-aminophenol or a derivative thereof, 2-aminophenol or a derivative thereof, 1,3-diaminobenzene or a derivative thereof, 1,2-diaminobenzene or a derivative thereof, dihydroxybenzene or a derivative thereof, trihydroxybenzene or a derivative thereof, a derivative of pyridine, a derivative of naphthalene, a derivative of morpholine, a derivative of quinoxaline, a derivative of pyrazole, a derivative of methylenedioxybenzene, 1,4-diaminobenzene or a derivative thereof, 1,2-diamino benzene or a derivative thereof, 4-aminophenol or a derivative thereof, 2-aminophenol or a derivative thereof, a heterocyclic hydrazone, a pyrimidine derivative, or an indole or an indoline derivative containing at least one hydroxy or amino group substituent.

27. (NEW) The composition of claim 26 wherein X is derived from an azo dye, 3-nitroaniline, 2-amino-4-nitroaniline, 2-nitro-1,4-diaminobenzene, a derivative of 2-nitro-1,4-diaminobenzene, a derivative of 4-nitro-2-aminophenol, a derivative of 2-nitro-4-aminophenol, a derivative of 2-nitroaniline, a derivative of quinoxaline, a derivative of anthraquinone, or a derivative of naphthoquinone.

28. (NEW) A hybrid dye corresponding to formula (I):



wherein X is a group derived from a substantive dye;

wherein Y is a group derived from (i) a primary intermediate oxidation dye precursor, (ii) a secondary intermediate oxidation dye precursor, or (iii) a precursor of melanin that is a derivative of an indole or an indoline; and

wherein S is a direct bond or a spacer group.

Docket No. H3170 PCT/US

Serial No. 10/031,740

Confirmation No. 8626

29. (NEW) The hybrid dye of claim 28 wherein Y is derived from 3-aminophenol or a derivative thereof, 2-aminophenol or a derivative thereof, 1,3-diaminobenzene or a derivative thereof, 1,2-diaminobenzene or a derivative thereof, dihydroxybenzene or a derivative thereof, trihydroxybenzene or a derivative thereof, a derivative of pyridine, a derivative of naphthalene, a derivative of morpholine, a derivative of quinoxaline, a derivative of pyrazole, a derivative of methylenedioxybenzene, 1,4-diaminobenzene or a derivative thereof, 1,2-diamino benzene or a derivative thereof, 4-aminophenol or a derivative thereof, 2-aminophenol or a derivative thereof, a heterocyclic hydrazone, a pyrimidine derivative, or an indole or an indoline derivative containing at least one hydroxy or amino group substituent.

30. (NEW) The the hybrid dye of claim 29 wherein X is derived from an azo dye, 3-nitroaniline, 2-amino-4-nitroaniline, 2-nitro-1,4-diaminobenzene, a derivative of 2-nitro-1,4-diaminobenzene, a derivative of 4-nitro-2-aminophenol, a derivative of 2-nitro-4-aminophenol, a derivative of 2-nitroaniline, a derivative of quinoxaline, a derivative of anthraquinone, or a derivative of naphthoquinone.

31. (NEW) A method of coloring keratin fibers comprising applying the hybrid dye of claim 28 to keratin fibers.

32. (NEW) A method of coloring human skin comprising applying the hybrid dye of claim 28 to human skin. --

Docket No. H3170 PCT/US
Serial No. 10/031,740
Confirmation No. 8626

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 13 to 32 will be pending after entry of the present amendment. Claim 1 is being canceled without prejudice.

Amendment

New Claims 13 to 32 replace original claims 1 to 12, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
13, 28	page 3, lines 4 to 19, page 6, lines 10 to 12, page 8, lines 23 to 25, page 10, lines 10 to 15.
14 to 17	page 16, lines 20 to 26, page 20, lines 5 to 6 and lines 28 to 30
18	page 26, lines 20 to 26, page 31, lines 8 to 9, page 33, lines 10 to 16, page 34, lines 6 to 15
19, 20	page 26, lines 20 to 26,
21, 22	page 31, lines 8 to 9, page 33, lines 10 to 16, page 34, lines 6 to 15
23, 27, 30	page 4, line 1 to page 5, line 20, pages 39 to 45.
24	pages 39 to 45
25	page 12, lines 27 to 28, page 13, lines 15 to 19
26, 29	page 6, line 13 to page 10, lines 23
31	page 38, lines 21 to 23
32	page 38, lines 24 to 28

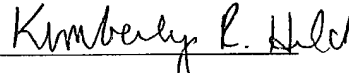
No new matter is added by the new claims.

Docket No. H3170 PCT/US
Serial No. 10/031,740
Confirmation No. 8626

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,



Kimberly R. Hild
(Reg. No. 39,224)
Attorney for Applicants
(610) 278-4964

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

Novel Dyes and Colorants

This invention relates to new dyes and dye precursors which are particularly suitable for coloring keratin fibers, to the use of these dyes and dye precursors and to colorants containing these dyes and/or dye precursors.

5 Among the various products available for the cosmetic treatment of the human body, formulations for modifying or shading the color of the hair occupy a prominent position. Disregarding blinding preparations which lighten the hair oxidatively by degrading the natural hair dyes, three types of colorants have long been of importance in the coloring of hair:

10 So-called oxidation colorants are used for permanent, intensive colors with corresponding fastness properties. Oxidation colorants normally contain oxidation dye precursors, so-called primary intermediates and secondary intermediates. The primary intermediates form the actual dyes with one another or by coupling with one or more secondary
15 intermediates under the influence of oxidizing agents or atmospheric oxygen.

Colorants or tints containing substantive dyes as their coloring component are normally used for temporary colors. Substantive dyes are based on dye molecules which are directly absorbed onto the hair and do
20 not require an oxidative process for developing the color. Dyes such as these include, for example, henna which has been used since ancient times for coloring the body and hair.

In recent years, a new coloring process has received considerable attention. In this process, precursors of the natural hair dye, melanin, more
25 particularly derivatives of indole or indoline, are applied to the hair and then form "nature-like" dyes in the hair in the course of oxidative processes. One such process using 5,6-dihydroxyindolines as the dye precursors is

Express Mail
Label No. EL015775445 US

5

melanin precursors for example.

10

20

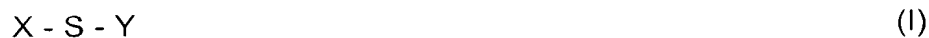
25

30

in many cases.

Substances such as these, which are referred to hereinafter as "hybrid dyes", are new.

In a first embodiment, therefore, the present invention relates to
5 hybrid dyes, more particularly for coloring keratin fibers, which correspond to formula (I):



10 where

X is a group derived from a substantive dye,

Y is a group derived from

- an oxidation dye precursor of the secondary or primary intermediate type,
- 15 - a derivative of indole or indoline as a precursor of melanin or
- a substantive dye and

S is a direct bond or a spacer group, with the proviso that S is not an alkylene, mono- or polyhydroxyalkylene group where Y is derived from a substantive dye.

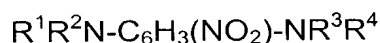
20 **DE-OSS 15 69 819** and **15 69 820** describe substantive nitro dyes formally composed of two aromatic systems attached by an alkylene or hydroxyalkylene bridge. These dyes have distinctly differing coloring properties from the two starting compounds due largely to the greater molecular weight. However, there is no reference whatever to be found in
25 either of these two documents to the teaching of the present invention.

The compounds corresponding to formula (I) are obtainable by standard synthesis methods of organic chemistry. In this connection, reference is specifically made to the Synthesis Examples in the following.

As mentioned above, the structural principles of known classes of
30 dyes form the basis of the newly developed hybrid dyes.

The group X is derived from compounds which may be assigned to the class of substantive dyes. Preferred classes of substantive dyes from which the group X is derived are:

- 2-Nitro-1,4-diaminobenzene and its derivatives corresponding to the following general formula:



in which the groups R^1 to R^4 independently of one another stand in particular for hydrogen, a C_{1-4} alkyl group, a C_{1-4} hydroxyalkyl group, a C_{2-4} dihydroxyalkyl group, a C_{1-4} aminoalkyl group, an optionally substituted phenyl group or a C_{3-8} cycloalkyl group.

Particularly preferred representatives of this class of dyes are the compounds known by the INCI names of HC Red No. 3, HC Blue No. 2, HC Blue No. 12 and HC Violet No. 1 and also 1,4-bis-(2'-hydroxyethyl)amino-2-nitrobenzene and 4-amino-2-nitrodiphenylamine-2'-carboxylic acid and 2-nitro-1,4-diaminobenzene.

- Derivatives of 4-nitro-2-aminophenol
Particularly preferred representatives are picramic acid and salts thereof, more particularly the sodium salt, 2-amino-6-chloro-4-nitrophenol and 2-chloro-6-ethylamino-4-nitrophenol.

- Derivatives of 2-amino-5-nitrophenol
A particularly preferred representative is the compound known by the INCI name of HC Violet No. 4.

- Derivatives of 2-nitro-4-aminophenol
Particularly preferred representatives are the compounds known under the INCI name of HC Red BN and 4-(2'-hydroxyethyl)-amino-2-nitrophenol.

- Derivatives of 2-nitroaniline
Particularly preferred representatives are the compounds known by

the INCI names of HC Yellow No. 2 and HC Yellow No. 6 and 4-ethylamino-3-nitrobenzoic acid and N-hydroxyethyl-2-nitro-4-methyl aniline and also 2,4-dinitroaniline.

- Derivatives of quinoxaline

5 A particularly preferred representative is 6-nitro-1,2,3,4-tetrahydro-quinoxaline.

- Derivatives of anthraquinone

Particularly preferred representatives are the compounds known by the INCI names of Disperse Blue 3, Disperse Violet 1 and Disperse
10 Violet 4 (CI 61105) and also 1-aminoanthraquinone and 1,4-diaminoanthraquinone-3-sulfonic acid.

- Derivatives of naphthoquinone

A particularly preferred representative is the compound known by the INCI name of Basic Blue 99

- 15 • Azo dyes

Particularly preferred representatives are the compounds known by the INCI names of Basic Yellow 57 (CI 12719), Disperse Orange 3 (CI 11005), Basic Red 76 (CI 12245), Disperse Black 9, Basic Brown 16 (CI 12250) and Basic Brown 17 (CI 12251).

20

With regard to other substantive dyes from which the group X may be derived, reference is also specifically made to the known reference books, for example Ch. Zviak, **The Science of Hair Care, Chapter 7 (pages 248-250)**, published as **Vol. 7 of the Series "Dermatology"**
25 (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986 and to the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel
30 e.V., Mannheim, Germany.

The groups X may of course also be derived from naturally occurring substantive dyes such as, for example, henna red, henna neutral, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet.

5 The group Y is a group derived from

- an oxidation dye precursor of the secondary or primary intermediate type,
- a derivative of indole or indoline as a precursor of melanin or
- a substantive dye.

10 In a first preferred embodiment of the present invention, the group Y is derived from an oxidation dye precursor of the secondary intermediate type.

Preferred classes of oxidation dye precursors of the secondary intermediate type from which the group Y may be derived are:

15 • 3-Aminophenol and derivatives thereof

Preferred representatives are 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 3-amino-6-methoxy-2-methylaminophenol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetyl-
 20 amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-dimethylaminophenol, 3-diethylaminophenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-ethylamino-4-methylphenol and 2,4-dichloro-3-aminophenol.

25

- 2-Aminophenol and derivatives thereof,
- 1,3-Diaminobenzene and derivatives thereof

Preferred representatives are 2,4-diaminophenoxyethanol, 1,3-bis-(2,4-diaminophenoxy)-propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2,4-diaminophenyl)-propane, 2,6-bis-
 30

(2-hydroxyethylamino)-1-methylbenzene, 1-amino-3-bis-(2' hydroxyethyl)-aminobenzene, 1,2-bis-(2,4-diaminophenoxy)-benzene and 1,3-bis-(2,4-diaminophenoxy)-benzene.

- 1,2-Diaminobenzene and derivatives thereof

5 Preferred representatives are 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene.

- Di- and trihydroxybenzenes and derivatives thereof

Preferred representatives are resorcinol, resorcinol monomethyl ether, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl
10 resorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene and also resorcinol dimethyl ether,

- Pyridine derivatives

Preferred representatives are 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine,
15 2,6-dihydroxy-3,4-diaminopyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxy-pyridine and 3,5-diamino-2,6-dimethoxypyridine.

- Naphthalene derivatives

20 Preferred representatives are 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene and also 1-aminonaphthalene.

- 25 • Morpholine derivatives

Preferred representatives are 6-hydroxybenzomorpholine and 6-aminobenzomorpholine.

- Quinoxaline derivatives

A preferred representative is 6-methyl-1,2,3,4-tetrahydroquinoxaline.

- 30 • Pyrazole derivatives

A preferred representative is 1-phenyl-3-methylpyrazol-5-one.

- Indole derivatives

Preferred representatives are 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole.

- 5 • Methylenedioxybenzene derivatives

Preferred representatives are 3,4-methylenedioxyphenol, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene.

- 10 • Heterocyclic compounds as disclosed in **WO 97/35550, WO 97/35552, WO 97/35553, WO 98/08485** and **WO 98/08486**, to which reference is expressly made.

With regard to other oxidation dye precursors of the secondary intermediate type from which the group Y may be derived, reference is also
 15 specifically made to the known reference books, for example Ch. Zviak, **The Science of Hair Care, Chapter 8 (pages 264-267)**, published as **Vol. 7 of the Series "Dermatology"** (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986 and to the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische
 20 Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim, Germany.

In a second preferred embodiment of the present invention, the group Y is derived from an oxidation dye precursor of the primary
 25 intermediate type.

Preferred classes of oxidation dye precursors of the primary intermediate type from which the group Y can be derived are:

- 1,4-Diaminobenzene and derivatives thereof

Preferred representatives are p-phenylenediamine, p-toluylenediamine, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-
 30

5 bis(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 1,3-bis-(N-(2-hydroxyethyl)-N-(4-aminophenylamino))-2-propanol, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane and 1,4-bis-(4-aminophenyl)-diazacycloheptane and corresponding
compounds with one or more halogen atoms, more particularly chlorine and fluorine, on the benzene ring.

- 1,2-Diaminobenzene and derivatives thereof
- 4-Aminopenol and derivatives thereof

10 Preferred representatives are p-aminophenol, 2-chloro-4-aminophenol, 4-amino-3-methylphenol, 2-hydroxyethylamino-4-aminophenol, 4,4'-diaminodiphenylamine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 4-amino-2-((diethylamino)-methyl)-phenol, bis-(2-hydroxy-5-aminophenyl)-methane, 4-amino-2-(2-hydroxyethoxy)-phenol.

- 15 • 2-Aminophenol and derivatives thereof
A preferred representative is o-aminophenol.

- Diaminopyridine derivatives
- Heterocyclic hydrazones
- 4-Aminopyrazole derivatives

20 Preferred representatives are 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone and 4,5-diaminopyrazole derivatives according to **EP 0 740 931** or **WO 94/08970** such as, for example, 4,5-diamino-1-(2'-hydroxyethyl)-pyrazole.

- Pyrimidine derivatives

25 Preferred representatives are 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2-dimethyl-amino-4,5,6-triaminopyrimidine.

30 With regard to other oxidation dye precursors of the primary

intermediate type from which the group Y may be derived, reference is also specifically made to the known reference books, for example Ch. Zviak, The Science of Hair Care, Chapter 8 (pages 264-267), published as Vol. 7 of the Series "Dermatology" (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986 and to the "Europäische Inventar der Kosmetik-Rohstoffe" published by the Europäische Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim, Germany.

10 In a third preferred embodiment of the present invention, the group Y is derived from a precursor of melanin selected from the derivatives of indole and indoline. In the context of the present invention, "precursors of melanin" are understood to be derivatives of indole and indoline which are capable of forming melanin dyes or corresponding melanin dye derivatives
15 in an oxidative process.

According to the invention, the groups Y in this embodiment are derived from indoles and indolines which contain at least one hydroxy or amino group, preferably as a substituent on the six-membered ring. These groups may carry other substituents, for example in the form of
20 etherification or esterification of the hydroxy group or alkylation of the amino group. Indoles and indolines containing two of these groups, particularly two hydroxy groups, of which one or both may be etherified or esterified are particularly preferred.

According to the invention, particularly preferred groups Y are
25 derived from derivatives of indoline, such as 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid, 5-hydroxyindoline, 6-hydroxyindoline, 5-aminoindoline, 6-aminoindoline and 4-aminoindoline.

30 Most particularly preferred groups Y are derivatives of 5,6-

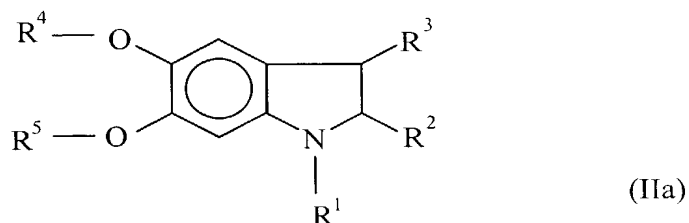
WO 01/02492

11

PCT/EP00/06159

dihydroxyindoline corresponding to formula (IIa):

5



in which - independently of one another -

10 R^1 is hydrogen, a C_{1-4} alkyl group, a C_{1-4} hydroxyalkyl group or a C_{3-6} cycloalkyl group,

R^2 is hydrogen or a $-COOH$ group which may even be present as a salt with a physiologically compatible anion,

R^3 is hydrogen or a C_{1-4} alkyl group,

15 R^4 is hydrogen, a C_{1-4} alkyl group or a group $-CO-R^6$ where R^6 is a C_{1-4} alkyl group or an optionally substituted phenyl group and

R^5 stands for one of the groups mentioned for R^4 .

According to the invention, preferred representatives are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline.

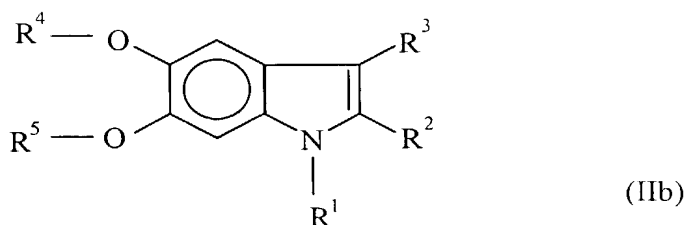
20 The parent compound, 5,6-dihydroxyindoline, is most particularly preferred.

According to the invention, preferred indoles from which the group Y is derived are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 5-hydroxyindole, 6-hydroxyindole, 5-aminoindole, 6-aminoindole and 4-aminoindole.

25

Particular preference is attributed to derivatives of 5,6-dihydroxyindole corresponding to formula (IIb):

30



in which - independently of one another -

R^1 is hydrogen, a C_{1-4} alkyl group, a C_{1-4} hydroxyalkyl group or a C_{3-6} cycloalkyl group,

5 R^2 is hydrogen or a $-COOH$ group which may even be present as a salt with a physiologically compatible anion,

R^3 is hydrogen, a C_{1-4} alkyl group or a group $-CH_2-NR^7R^8$, where R^7 and R^8 independently of one another are hydrogen or a C_{1-4} alkyl group,

R^4 is hydrogen, a C_{1-4} alkyl group or a group $-CO-R^6$ where R^6 is a C_{1-4} alkyl group or an optionally substituted phenyl group and

10 R^5 stands for one of the groups mentioned for R^4 .

According to the invention, preferred representatives are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole. The parent compound, 5,6-dihydroxyindole, is most particularly preferred.

15 In a fourth embodiment of the present invention, the group Y derives from a substantive dye. Suitable and preferred dyes Y are derived in principle from the same compounds that are described in detail above in the definition of the group X.

20 Although, according to the invention, compounds where the groups X and Y are identical are not intended to be excluded from the defined group of hybrid dyes, the compounds according to this embodiment normally contain different groups X and Y. More particularly, the groups X and Y differ in their light absorption capacity to the extent that the wavelengths of the absorption maxima of the two groups differ by at least
25 30 nm, preferably by at least 50 nm and more particularly by at least 80 nm.

In a first embodiment of the invention, the group S in structural formula (I) stands for a direct bond.

30 In such cases, the π -electron systems of the groups X and Y will generally interact so that the light absorption behavior of the hybrid dye

generally differs distinctly from that of the groups X and Y. As a result, a significantly different color tone is obtained on the hair by comparison with colors formed with a mixture of corresponding dyes which correspond to the groups X and Y.

- 5 However, a core object of the present invention is to avoid the problems arising in many areas where complex dye mixtures are used, for example in regard to absorptivity and fastness to washing, without altering either the color tone or the shade.

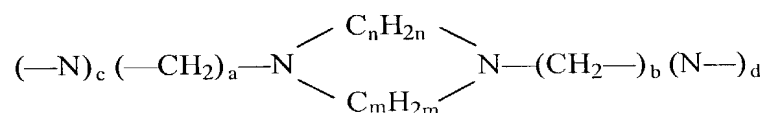
10 According to the invention, therefore, it is generally preferred for S to be a spacer group through which no interaction between the π -electron systems of the groups X and Y occurs. Accordingly, S preferably contains at least one carbon atom with sp^3 hybridization on the direct connecting line between the groups X and Y.

Preferred spacer groups are:

- 15 • Alkylene groups corresponding to the general formula $-C_nH_{2n}-$, more particularly $-(CH_2)_n-$, in which n is an integer, preferably a number of 1 to 8 and more particularly a number of 1 to 4.
- According to the invention, preferred alkylene groups are the methylene, 1,2-ethylene and 1,3-propylene group.
- 20 • Cycloaliphatic groups, such as cyclopentyl, cyclohexyl and cycloheptyl groups.
- Mono- and polyhydroxyalkylene groups corresponding to the general formula $-C_nH_{2n-x}(OH)_x$, in which n is an integer, preferably a number of 1 to 8 and more particularly a number of 1 to 4 and x is an integer,
- 25 more particularly a number of 1 to 3.
- Preferred hydroxyalkylene groups are the hydroxymethylene, hydroxy-1,2-ethylene, 2-hydroxy-1,3-propylene, 2,3-dihydroxy-1,3-propylene and 2,3- or 1,4-dihydroxybutylene group.
- Dialkyleneamino groups optionally substituted at the alkyl chains,
- 30 more particularly those corresponding to the general formula

$-(CH_2)_n-N(Z)-(CH_2)_m-$, in which n and m independently of one another represent an integer of 1 to 8, more particularly 1 to 4, but are preferably the same number, and Z represents hydrogen, a C₁₋₈ and more particularly C₁₋₄ alkyl group, a C₁₋₈ and more particularly C₁₋₄ monohydroxyalkyl group, a C₂₋₈ and more particularly C₂₋₄ dihydroxyalkyl group or a C₃₋₈ and more particularly C₃₋₄ trihydroxyalkyl group, and those corresponding to the following general formula:

10



15

in which a and b independently of one another represent integers of 0 to 4 and c and d stand for 0 or 1, with the proviso that c = 0 when a = 0 and d = 0 when b = 0, n is an integer of 1 to 5 and m is an integer of 1 to 3, with the proviso that the sum n + m = 3 to 8. The 1,4-piperazino group is particularly preferred.

20

- Trialkylenediamino groups optionally substituted at the alkyl chains, more particularly those corresponding to the general formula: $-(CH_2)_n-N(Z)-(CH_2)_m-N(A)-(CH_2)_p-$, in which n, m and p independently of one another may represent an integer of 1 to 8 and more particularly 1 to 4, although n and m preferably stand for the same number, and Z and A independently of one another represent hydrogen, a C₁₋₈ and more particularly C₁₋₄ alkyl group, a C₁₋₈ and more particularly C₁₋₄ monohydroxyalkyl group, a C₂₋₈ and more particularly C₂₋₄ dihydroxyalkyl group or a C₃₋₈ and more particularly C₃₋₄ trihydroxyalkyl group.

25

30

- Ether groups optionally substituted at the alkyl chains, more particularly those corresponding to the general formula $-(CH_2)_n-O-$

$(CH_2)_m-$, in which n and m independently of one another may represent an integer of 1 to 8 and more particularly 1 to 4, but preferably stand for the same number,

- 5 • Polyether groups optionally substituted at the alkyl chains, more particularly those corresponding to the general formula $-(CH_2)_n-O-(CH_2)_m-O-(CH_2)_n-$, in which n and m independently of one another may represent an integer of 1 to 8 and more particularly 1 to 4, but preferably stand for the same number,
- 10 • Sulfur-containing groups, more particularly groups corresponding to the general formula $-(CH_2)_n-S(O)_o-(CH_2)_m-$ in which n and m independently of one another may represent an integer of 1 to 8 and more particularly 1 to 4, but preferably stand for the same number, and o is the number 0, 1 or 2.

15 The spacers S in the hybrid dyes according to the invention are attached by their two free bonds to the groups X and Y so that they each replace a hydrogen atom as substituent in the dye or dye precursor molecules on which the groups X and Y are based.

In a first preferred embodiment, the spacer group replaces a
20 hydrogen atom directly attached to a ring system of the group X or Y as substituent. Examples of such ring systems are

- aromatic and cycloaliphatic hydrocarbon ring systems, more particularly benzene, naphthalene, anthracene, naphthoquinone and
25 anthraquinone systems
- heterocyclic ring systems, more particularly pyridine, pyrazole, pyrimidine, indole and indoline systems.

In a second preferred embodiment, the spacer group S replaces a
30 hydrogen atom of a primary or secondary amino group attached to an

WO 01/02492

16

PCT/EP00/06159

aromatic, cycloaliphatic or heterocyclic ring system either directly or through an aliphatic hydrocarbon group as substituent.

In a third embodiment, the spacer group S replaces the hydrogen atom of a hydroxy group attached to an aromatic, cycloaliphatic or heterocyclic ring system either directly or through an aliphatic hydrocarbon group as substituent.

The hybrid dyes according to the invention are eminently suitable for coloring keratin fibers. Keratin fibers in the context of the invention are pelts, wool, feathers and in particular human hair. However, there is nothing to prevent them being used in other fields, particularly color photography.

Accordingly, in a second embodiment, the present invention relates to compositions for coloring keratin fibers, more particularly human hair, which contain a hybrid dye corresponding to structural formula (I). The teaching according to the invention does of course also encompass compositions containing combinations of more than one hybrid dye corresponding to formula (I).

The compositions according to the invention for coloring human hair may also contain any of the ingredients typical of such compositions.

The colorants according to the invention preferably contain at least one other dye, one other dye precursor and/or an indole or indoline derivative as melanin precursor.

In a first embodiment, colorants which contain at least one oxidation dye precursor besides a hybrid dye of formula (I) are particularly preferred. These oxidation dye precursors may be both of the secondary intermediate type and of the primary intermediate type.

Suitable oxidation dye precursors of the primary intermediate type are, for example, primary aromatic amines with another free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazole derivatives and

2,4,5,6-tetraaminopyrimidine and derivatives thereof.

According to the invention, preferred primary intermediates are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 2-chloro-4-aminophenol, o-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone, 4-amino-3-methylphenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2-hydroxyethylaminomethyl-4-aminophenol, 4,4'-diaminodiphenylamine, 4-amino-3-fluorophenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 4-amino-2-((diethylamino)-methyl)-phenol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,4-bis-(4-aminophenyl)-diazacycloheptane, 1,3-bis-(N-(2-hydroxyethyl)-N-(4-aminophenylamino))-2-propanol, 4-amino-2-(2-hydroxyethoxy)-phenol, 1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane and 4,5-diaminopyrazole derivatives according to **EP 0 740 931** and **WO 94/08970** such as, for example, 4,5-diamino-1-(2'-hydroxyethyl)-pyrazole. Particularly preferred primary intermediates are p-phenylenediamine, p-toluylenediamine, p-aminophenol, 1-(2'-hydroxyethyl)-2,5-diaminobenzene, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2,4,5,6-tetraaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine and 4-hydroxy-2,5,6-triaminopyrimidine.

Suitable oxidation dye precursors of the secondary intermediate type are, for example, m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives.

According to the invention, preferred secondary intermediates are

- m-aminophenol and derivatives thereof such as, for example, 5-amino-2-methylphenol, 5-(3-hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxy ethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetyl-amino-2-

- chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, 3-(dimethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-(ethylamino)-4-methylphenol and 2,4-dichloro-3-aminophenol,
- 5 - o-aminophenol and derivatives thereof, such as 4-chloro-o-aminophenol,
- m-diaminobenzene and derivatives thereof such as, for example, 2,4-diaminophenoxyethanol, 1,3-bis-(2,4-diaminophenoxy)-propane,
- 10 1-methoxy-2-amino-4-(2'-hydroxyethylamino)-benzene, 1,3-bis-(2,4-diaminophenyl)-propane, 2,6-bis-(2-hydroxyethylamino)-1-methylbenzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,
- o-diaminobenzene and derivatives thereof such as, for example, 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,
- 15 - di- and trihydroxybenzene derivatives such as, for example, resorcinol, resorcinol monomethyl ether, 2-methyl resorcinol, 5-methyl resorcinol, 2,5-dimethyl resorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,
- pyridine derivatives such as, for example, 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-3,4-diaminopyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
- 20 - naphthalene derivatives such as, for example, 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene,
- 30 - morpholine derivatives such as, for example, 6-hydroxybenzo-

- to use a hybrid dye of formula (I) containing a group Y derived from an oxidation dye precursor of the secondary intermediate type in combination with at least one other oxidation dye precursor of the primary intermediate type,
- to use a hybrid dye of formula (I) containing a group Y derived from an oxidation dye precursor of the primary intermediate type in combination with at least one other oxidation dye precursor of the secondary intermediate type
- to use a hybrid dye of formula (I) containing a group Y derived from an oxidation dye precursor of the primary intermediate type in combination with at least one other oxidation dye precursor of the primary intermediate type

derivative of indole or indoline as a melanin precursor in combination with at least one other oxidation dye precursor of the secondary intermediate type.

5 In a second embodiment, preferred colorants contain at least one substantive dye in addition to a hybrid dye of formula (I).

Substantive dyes suitable for use in accordance with the invention are, for example, nitrophenylenediamines, nitroaminophenols, azo dyes, anthraquinones and indophenols. Preferred substantive dyes are the
10 compounds known under the International names or commercial names of HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, HC Blue 12, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17
15 and also 1,4-bis-(β -hydroxyethyl)-amino-2-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, hydroxyethyl-2-nitrotoluidine, picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene. The cationic substantive dyes marked under the
20 name of Arianor® are particularly preferred substantive dyes.

The compositions according to the invention may also contain naturally occurring dyes such as, for example, henna red, henna neutral, camomile blossom, sandalwood, black tea, black alder bark, sage, logwood, madder root, catechu, sedre and alkanet.

25 The compositions according to the invention of this embodiment contain the substantive dyes in a quantity of preferably 0.01 to 20% by weight, based on the colorant as a whole.

In a third embodiment, colorants which contain at least one derivative of indole or indoline as a melanin precursor in addition to a
30 hybrid dye of formula (I) are particularly preferred.

30 R^5 stands for one of the groups mentioned for R^4 ,

WO 01/02492

22

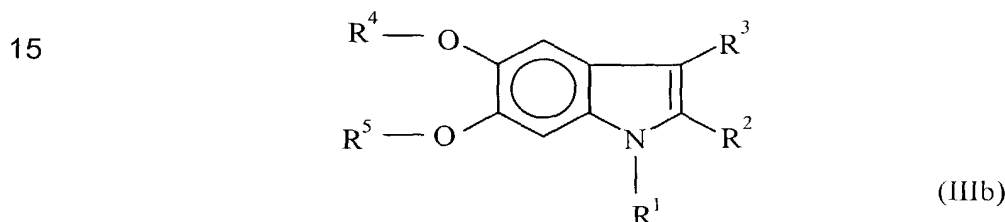
PCT/EP00/06159

or a physiologically compatible salt of these compounds with an organic or inorganic acid.

According to the invention, preferred representatives are 5,6-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline. The parent compound, 5,6-dihydroxyindoline, is most particularly preferred.

According to the invention, preferred indoles are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxyindole-2-carboxylic acid, 5-hydroxyindole, 6-hydroxyindole, 5-aminoindole, 6-aminoindole and 4-aminoindole.

Particular preference is attributed to derivatives of 5,6-dihydroxyindole corresponding to formula (IIIb):



20 in which - independently of one another -

R^1 is hydrogen, a C_{1-4} alkyl group, a C_{1-4} hydroxyalkyl group or a C_{3-6} -cycloalkyl group,

R^2 is hydrogen or a $-COOH$ group which may even be present as a salt with a physiologically compatible anion,

25 R^3 is hydrogen, a C_{1-4} alkyl group or a group $-CH_2-NR^7R^8$ where R^7 and R^8 independently of one another represent hydrogen or a C_{1-4} alkyl group,

R^4 is hydrogen, a C_{1-4} alkyl group or a group $-CO-R^6$ where R^6 is a C_{1-4} alkyl group or an optionally substituted phenyl group and

R^5 stands for one of the groups mentioned for R^4 ,

30 or a physiologically compatible salt of these compounds with an organic or

inorganic acid.

According to the invention, preferred representatives are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole. The
5 parent compound, 5,6-dihydroxyindole, is most particularly preferred.

The present invention does of course also encompass compositions containing more than one indoline or indole derivative or mixtures of indoline and indole derivatives.

The indole or indoline derivatives are present in the compositions
10 according to the invention in quantities of normally 0.05 to 10% by weight and preferably 0.2 to 5% by weight.

In this embodiment, it may be preferred

- to use a hybrid dye of formula (I) containing a group Y derived from an oxidation dye precursor of the secondary intermediate type in
15 combination with at least one derivative of indole or indoline as a precursor of melanin,
- to use a hybrid dye of formula (I) containing a group Y derived from an oxidation dye precursor of the primary intermediate type in
20 combination with at least one derivative of indole or indoline as a precursor of melanin.

In the embodiments mentioned, the oxidation dye precursors, substantive dyes or melanin precursors do not have to be single compounds. Instead, the hair colorants according to the invention - due to
25 the processes used for producing the individual dyes - may contain small quantities of other components providing they do not adversely affect the coloring result or have to be ruled out for other reasons, for example toxicological reasons.

The hybrid dyes, secondary intermediates and primary intermediates
30 containing amino groups and the indoline and indole derivatives may be

used both as free bases and in the form of their physiologically compatible salts with inorganic or organic bases, for example hydrochlorides, sulfates and hydrobromides.

With regard to the dyes suitable for use in the hair coloring and tinting formulations according to the invention, reference is also specifically
5 made to Ch. Zviak's work The Science of Hair Care, Chapter 7 (pages 248-250; Substantive Dyes) and Chapter 8, pages 264-267; Oxidation Dye Precursors), published as Vol. 7 of the Series "Dermatology" (Editors: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York/Basel, 1986 and to
10 the **"Europäische Inventar der Kosmetik-Rohstoffe"** published by the Europäische Gemeinschaft and available on floppy disk from the Bundesverband Deutscher Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim, Germany.

15 In a preferred variant of this embodiment, compositions according to the invention containing a hybrid dye of formula (I) in which the group Y derives from a melanin precursor of the indole or indoline type contain no dyes or dye precursors other than the hybrid dyes mentioned.

In another preferred variant, compositions according to the invention
20 containing a hybrid dye of formula (I), in which the group Y derives from a melanin precursor of the indole or indoline type, and/or a melanin precursor additionally contain at least one amino acid or oligopeptide.

Amino acids in the context of the invention are substances which contain at least one amino group and at least one -COOH or -SO₃H group.

25 Preferred amino acids are aminocarboxylic acids, more particularly α -aminocarboxylic acids and ω -aminocarboxylic acids. Among the α -aminocarboxylic acids, arginine, lysine, ornithine and histidine are particularly preferred.

The amino acids are preferably added to the formulations according
30 to the invention in free form. However, the amino acids may also be used

in salt form. Preferred salts are the compounds containing hydrohalic acids, more particularly hydrochlorides and hydrobromides.

Particularly preferred amino acids are lysine and particularly arginine used in particular in free form but also as the hydrochloride.

5 In addition, the amino acids may also be used in the form of oligopeptides and protein hydrolyzates providing steps are taken to ensure that the necessary quantities of compounds conforming to the definition of amino acids according to the invention are present. Reference is expressly made in this connection to the disclosure of **DE-OS 22 15 303**.

10 The present invention does of course also encompass compositions containing two or more amino acids or oligopeptides. Combinations of arginine with another amino acid or an oligopeptide are preferred.

The compositions according to the invention contain the amino acid or oligopeptide in quantities of preferably 0.1 to 10% by weight and more
15 preferably 1 to 4% by weight, based on the composition as a whole.

Hair colorants, more particularly those where the color is developed oxidatively with atmospheric oxygen or other oxidizing agents, such as hydrogen peroxide, are normally adjusted to a mildly acidic or alkaline pH value, i.e. to a pH value in the range from about 5 to 11. To this end, the
20 colorants contain alkalizing agents, normally alkali metal or alkaline earth metal hydroxides, ammonia or organic amines.

In one special embodiment of the present invention, the amino acid or the oligopeptide is used not only to intensify color development, but also at least partly as an alkalizing agent. Accordingly, amino acids and
25 oligopeptides of which 2.5% by weight solutions in water have a pH value of 9 or higher are preferably used in this embodiment. Such amino acids are the preferred compounds arginine and lysine. In this particular embodiment, the other alkalizing agent is preferably selected from the group consisting of monoethanolamine, monoisopropanolamine, 2-amino-
30 2-methylpropanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-

propanediol, 2-amino-2-methylbutanol and triethanolamine and alkali metal and alkaline earth metal hydroxides. Within this group, monoethanolamine, triethanolamine and 2-amino-2-methylpropanol and 2-amino-2-methyl-1,3-propanediol are particularly preferred. ω -Amino acids, such as ω -aminocaproic acid, are also preferably used as alkalizing agents in this embodiment of the invention.

Particularly advantageous properties are exhibited by formulations in which the amino acid or the oligopeptide and the other alkalizing agent are present in a ratio by weight of 1:5 to 5:1. Quantity ratios of 1:2 to 2:1 have proved to be particularly suitable.

To produce the colorants according to the invention, the compulsory and optional constituents mentioned above are incorporated in a suitable water-containing carrier. Such carriers are, for example, cremes, emulsions, gels or even surfactant-containing foaming solutions, for example shampoos, foam aerosols or other preparations suitable for application to the hair. These preparations are adjusted to a pH value of preferably 5 to 11 and, more preferably, 7 to 10 with the above-mentioned alkalizing agents or suitable acids such as, in particular, food-grade acids, such as citric acid, tartaric acid, lactic acid and acetic acid.

The colorants according to the invention may also contain any of the known active substances, additives and auxiliaries typical of such preparations. In many cases, the colorants contain at least one surfactant, both anionic and zwitterionic, ampholytic, nonionic and cationic surfactants being suitable in principle. In many cases, however, it has been found to be of advantage to select the surfactants from anionic, zwitterionic or nonionic surfactants. Anionic surfactants can be particularly useful.

Suitable anionic surfactants for the hair colorants according to the invention are any anionic surface-active substances suitable for use on the human body. Such substances are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate or

phosphate group and a lipophilic alkyl group containing around 10 to 22 carbon atoms. In addition, glycol or polyglycol ether groups, ether, amide and hydroxyl groups and - generally - ester groups may also be present in the molecule. The following are examples of suitable anionic surfactants -

- 5 in the form of the sodium, potassium and ammonium salts and the mono-, di- and trialkanolammonium salts containing 2 or 3 carbon atoms in the alkanol group:
 - linear and branched fatty acids containing 8 to 22 carbon atoms (soaps),
 - 10 - ether carboxylic acids corresponding to the formula $R-O-(CH_2-CH_2O)_x-CH_2-COOH$, in which R is a linear alkyl group containing 10 to 22 carbon atoms and $x = 0$ or 1 to 16,
 - acyl sarcosides containing 10 to 18 carbon atoms in the acyl group,
 - acyl taurides containing 10 to 18 carbon atoms in the acyl group,
 - 15 - acyl isethionates containing 10 to 18 carbon atoms in the acyl group,
 - sulfosuccinic acid mono- and dialkyl esters containing 8 to 18 carbon atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,
 - 20 - linear alkane sulfonates containing 12 to 18 carbon atoms,
 - linear α -olefin sulfonates containing 12 to 18 carbon atoms,
 - α -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms,
 - alkyl sulfates and alkyl polyglycol ether sulfates corresponding to the
 - 25 formula $R-O(CH_2-CH_2O)_x-SO_3H$, in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and $x = 0$ or 1 to 12,
 - mixtures of surface-active hydroxysulfonates according to **DE-A-37 25 030**,
 - sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene
 - 30 glycol ethers according to **DE-A-37 23 354**,

- sulfonates of unsaturated fatty acids containing 12 to 24 carbon atoms and 1 to 6 double bonds according to **DE-A-39 26 344**,
- esters of tartaric acid and citric acid with alcohols in the form of addition products of around 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule and, in particular, salts of saturated and, more particularly, unsaturated C₈₋₂₂ carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

In the context of the invention, zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one -COO⁽⁻⁾ or -SO₃⁽⁻⁾ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminoethyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminoethyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and cocoacylaminoethyl hydroxyethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known by the CTFA name of Cocamidopropyl Betaine.

Ampholytic surfactants are surface-active compounds which, in addition to a C₈₋₁₈ alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO₃H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkyl aminobutyric acids, N-alkyl iminodipropionic acids, N-hydroxyethyl-N-alkyl amidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkyl aminopropionic acids and alkyl

aminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl amino-propionate, cocoacyl aminoethyl aminopropionate and C₁₂₋₁₈ acyl sarcosine.

5 Nonionic surfactants contain, for example, a polyol group, a poly-alkylene glycol ether group or a combination of polyol and polyglycol ether groups as the hydrophilic group. Examples of such compounds are

- products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide onto linear fatty alcohols containing 8 to 22 carbon atoms, onto fatty acids containing 12 to 22 carbon atoms and onto alkylphenols containing 8 to 15 carbon atoms in the alkyl group,
- C₁₂₋₂₂ fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide onto glycerol,
- C₈₋₂₂ alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- 15 - products of the addition of 5 to 60 moles of ethylene oxide onto castor oil and hydrogenated castor oil,
- products of the addition of ethylene oxide onto sorbitan fatty acid esters,
- products of the addition of ethylene oxide onto fatty acid alkanolamides.

Examples of cationic surfactants suitable for use in the hair treatment preparations according to the invention are, in particular, quaternary ammonium compounds. Preferred quaternary ammonium compounds are ammonium halides, such as alkyl trimethyl ammonium chlorides, dialkyl dimethyl ammonium chlorides and trialkyl methyl ammonium chlorides, for example cetyl trimethyl ammonium chloride, 20 stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dimethyl ammonium chloride, lauryl dimethyl benzyl ammonium chloride and tricetyl methyl ammonium chloride. Other cationic surfactants suitable for use in accordance with the invention are the quaternized protein hydrolyzates.

30 Also suitable for use in accordance with the invention are cationic

25 The surfactants representing addition products of ethylene and/or
propylene oxide with fatty alcohols or derivatives of these addition products
may be both products with a "normal" homolog distribution and products
with a narrow homolog distribution. Products with a "normal" homolog
distribution are mixtures of homologs which are obtained in the reaction of
30 fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides

or alkali metal alcoholates as catalysts. By contrast, narrow homolog distributions are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrow homolog distribution can be of advantage.

According to the invention, the use of anionic surfactants in combination with zwitterionic surfactants can be particularly preferred.

According to the invention, compositions additionally containing a cationic polymer are also preferred.

Among the cationic polymers, the permanently cationic polymers are preferred. According to the invention, "permanently cationic polymers" are polymers which contain a cationic group irrespective of the pH of the composition. These are generally polymers which contain a quaternary nitrogen atom, for example in the form of an ammonium group. Preferred cationic polymers are, for example,

- the quaternized cellulose derivatives commercially available under the names of Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and Polymer JR® 400 are preferred quaternized cellulose derivatives,
- polysiloxanes containing quaternary groups such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl silyl amodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone which is also known as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethyl siloxanes, Quaternium-80),
- cationic guar derivatives such as, in particular, the products marketed under the names of Cosmedia® Guar and Jaguar®,
- polymeric dimethyl diallyl ammonium salts and copolymers thereof with

esters and amides of acrylic acid and methacrylic acid. The products commercially available under the names of Merquat® 100 (poly(dimethyl diallylammonium chloride)) and Merquat® 550 (dimethyl diallylammonium chloride/acrylamide copolymer) are examples of such cationic polymers,

- copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate such as, for example, vinyl pyrrolidone/dimethylamino methacrylate copolymers quaternized with diethyl sulfate. Such compounds are commercially available under the name of Gafquat® 734 and Gafquat® 755,
 - The vinyl pyrrolidones/vinyl imidazolinium methochloride copolymers commercially available under the name of Luviquat® FC 370, FC 550, FC 905 and HM 552,
 - quaternized polyvinyl alcohol;
- and the polymers containing quaternary nitrogen atoms in the main polymer chain known under the names of
- Polyquaternium 2,
 - Polyquaternium 17,
 - Polyquaternium 18 and
 - Polyquaternium 27.

Other suitable cationic polymers are the polymers known by the names of Polyquaternium-24 (commercial product: Quatrisoft® LM 200 for example), Polyquaternium-32, Polyquaternium-35 and Polyquaternium-37 (commercial products: Salcare® SC 92 and Salcare® SC 95). Also suitable for use in accordance with the invention are the vinyl pyrrolidone copolymers known by the commercial names of Copolymer 845 (manufacturer: ISP), Gaffix® VC 713 (manufacturer: ISP), Gafquat® ASCP 1011, Gafquat® HS 110, Luviquat® 8155 and Luviquat® MS 370.

According to the invention preferred cationic polymers are

quaternized cellulose derivatives, polymeric dimethyl diallyl ammonium salts, Polyquaternium-27 and copolymers thereof and polymers of the Polyquaternium-2 type. Cationic cellulose derivatives, more particularly the commercial product Polymer® JR 400, and polymers of the
5 Polyquaternium-2 type, more particularly the commercial product Mirapol® A-15, are most particularly preferred cationic polymers.

The cationic polymers are present in the compositions according to the invention in quantities of preferably 0.05 to 5% by weight, based on the composition as a whole.

10 In many cases, amphopolymers may also be used as an alternative to the cationic polymers. Amphopolymers are amphoteric polymers, i.e. polymers which contain both free amino groups and free -COOH or -SO₃H groups in the molecule and which are capable of forming inner salts, zwitterionic polymers which contain quaternary ammonium groups and
15 -COO⁻ or -SO₃⁻ groups in the molecule and polymers which contain -COOH- or SO₃H groups and quaternary ammonium groups. One example of an amphopolymer suitable for use in accordance with the invention is the acrylate resin commercially available as Amphomer® which is a copolymer of tert.butylaminoethyl methacrylate, N-(1,1,3,3-
20 tetramethylbutyl)-acrylamide and two or more monomers from the group consisting of acrylic acid, methacrylic acid and simple esters thereof. Other preferred amphopolymers consist of unsaturated carboxylic acids (for example acrylic and methacrylic acid), cationically derivatized unsaturated carboxylic acids (for example acrylamidopropyl trimethyl ammonium
25 chloride) and optionally other ionic or nonionic monomers of the type disclosed, for example, in **DE-OS 39 29 973** and the prior art literature cited therein. According to the invention, terpolymers of acrylic acid, methyl acrylate and methacrylamidopropyl trimonium chloride, which are commercially available under the name of Merquat® 2001 N, and the
30 commercial product Merquat® 280 may also be used as amphopolymers.

The compositions according to the invention also contain at least one nonionic or anionic polymer with thickening properties, preferably optionally crosslinked polyacrylic acids, cellulose derivatives, for example methyl cellulose, hydroxyalkyl cellulose and carboxymethyl cellulose, and xanthan gum.

Other active substances, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,
- 10 - anionic polymers such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.butyl
- 15 acrylamide terpolymers,
- thickeners, such as agar agar, guar gum, alginates, gum arabic, karaya gum, locust bean gum, linseed gums, dextrans, starch fractions and derivatives, such as amylose, amylopectin and dextrans, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for
- 20 example, polyvinyl alcohol,
- structurants, such as glucose, maleic acid and lactic acid,
- hair-conditioning compounds, such as phospholipids, for example soybean lecithin, egg lecithin and kephalins, and also silicone oils,
- protein hydrolyzates, more particularly elastin, collagen, keratin, milk
- 25 protein, soybean protein and wheat protein hydrolyzates, condensation products thereof with fatty acids and quaternized protein hydrolyzates,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol, diethylene glycol, ethoxybutanol and
- 30 butoxyethanol and also benzyl alcohol,

WO 01/02492

35

PCT/EP00/06159

- antidandruff agents, such as Piroctone Olamine and Zinc Omadine,
- other substances for adjusting the pH value, such as for example α - and β -hydroxycarboxylic acids,
- active principles, such as panthenol, pantothenic acid, allantoin,
- 5 pyrrolidone carboxylic acids and salts thereof, plant extracts and vitamins,
- cholesterol,
- UV filters,
- consistency factors, such as sugar esters, polyol esters or polyol alkyl
- 10 ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- 15 - swelling and penetration agents, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogen carbonates, guanidines, ureas and primary, secondary and tertiary phosphates,
- opacifiers, such as latex,
- pearlizers, such as ethylene glycol mono- and distearate,
- 20 - propellents, such as propane/butane mixtures, N₂O, dimethyl ether, CO₂ and air and
- antioxidants.

To produce the colorants according to the invention, the constituents

25 of the water-containing carrier are used in the usual quantities for this purpose. For example, emulsifiers are used in concentrations of 0.5 to 30% by weight while thickeners are used in concentrations of 0.1 to 25% by weight, based on the colorant as a whole.

Information on the other constituents of the colorants according to

30 the invention can be found in the reference books known to the expert, for

example Umbach, **Kosmetik, 2nd Edition, Georg Thieme Verlag, Stuttgart/New York, 1995** and Kh. Schrader, **Grundlagen und Rezepturen der Kosmetika, 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989.**

5 Known processes may be used to develop the color on the keratin fiber.

Hair colorants containing one or more hybrid dyes in which the groups X and Y are derived from substantive dyes and which contain no other dye precursors may be applied to the hair in the same way as
10 conventional tinting preparations. These preparations are normally washed off after a certain contact time and the hair is optionally subjected to an aftertreatment. However, where it is used in a hair mascara, the colorant may also be applied to the hair, but especially to individual hair tresses, with an application aid and left on the hair.

15 In another embodiment, the color is developed with atmospheric oxygen as sole oxidizing agent. This embodiment is particularly preferred when the group Y of the hybrid dye is derived from a melanin precursor or "air-oxidizable" primary and secondary intermediates or when the compositions contains melanin precursors and/or "air-oxidizable" oxidation
20 dye precursors of the primary or secondary intermediate type. In the context of the invention, air-oxidizable compounds are compounds or dye precursors where oxidative development of the final color can be carried out solely with atmospheric oxygen, i.e. without using typical chemical oxidizing agents. Triaminobenzene derivatives are examples of such air-
25 oxidizable compounds.

The use of a chemical oxidizing agent can be preferred in many cases, particularly in cases where the group Y of the hybrid dye derives from a melanin precursor or primary or secondary intermediates or where the composition contains melanin precursors and/or dye precursors of the
30 primary or secondary intermediate type. The same also applies when the

hair is not only to be colored, but also lightened. In such cases, a particularly suitable oxidizing agent is hydrogen peroxide or an addition product thereof onto urea, melamine or sodium borate.

5 The preparation of the oxidizing agent is preferably mixed with the preparation containing the dye precursors immediately before colouring of the hair. The ready-to-use hair colouring preparation formed should preferably have a pH value of 5 to 11. In a particularly preferred embodiment, the hair colorant is used in a mildly alkaline medium. The application temperatures may be in the range from 15 to 40°C and are
10 preferably at the temperature of the scalp. After a contact time of ca. 5 to 45 and more particularly 15 to 30 minutes, the hair colorant is rinsed out from the hair to be colored. There is no need to wash the hair with a shampoo if a high-surfactant carrier, for example a colouring shampoo, has been used.

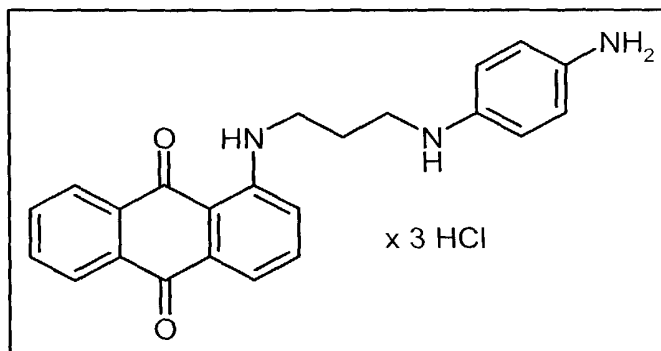
15 The preparation containing the dye precursors may be applied to the hair without premixing with the oxidation component, particularly where the hair is difficult to dye. After a contact time of 20 to 30 minutes, the oxidation component is applied, optionally after rinsing. After a further contact time of 10 to 20 minutes, the hair is rinsed and if desired washed
20 with shampoo. In a first variant of this embodiment where the previous application of the dye precursors is intended to produce better penetration into the hair, the corresponding preparation is adjusted to a pH of about 4 to 7. In a second variant, oxidation with air is carried out first, the preparation applied preferably having a pH of 7 to 10. In the subsequent
25 accelerated post-oxidation step, it may be preferred to use acidified peroxydisulfate solutions as the oxidizing agent. In one particular embodiment of this process, the final color is developed by repeated application of the preparation followed each time by oxidation with air. The preparation is preferably applied at intervals of about one day to about two
30 weeks. Special shades can be obtained very selectively in this way.

Examples

1. Syntheses

1.1. 1-((3-((4-aminophenyl)-amino)-propyl)-amino)-anthracene-9,10-dione (hybrid dye A)

5



X derived from a substantive dye (1-aminoanthracene-9,10-dione)

Y derived from an oxidation dye precursor of the primary intermediate type (p-phenylenediamine)

10 S. alkylene group (-CH₂-CH₂-CH₂-)

1st Stage

A mixture of 3.73 g (0.015 mole) of 1-chloroanthraquinone, 3.00 g (0.015 mole) of N-(p-nitrophenyl)-propylenediamine, 1.54 g (0.011 mole) of potassium carbonate and 0.13 g of Cu powder in 40 ml of DMSO was reacted with stirring under nitrogen for 1.5 h at 120 - 130°C. After cooling, the residue was filtered off and recrystallized from acetone/water. 1-((3-((4-aminophenyl)-amino)-propyl)-amino)-anthracene-9,10-dione (melting point: 183-185°C), a red powder, was obtained in a yield of 1.4 g.

20

2nd Stage

A solution of 1.00 g (2.4 mmoles) of 1-((3-((4-aminophenyl)-amino)-

WO 01/02492

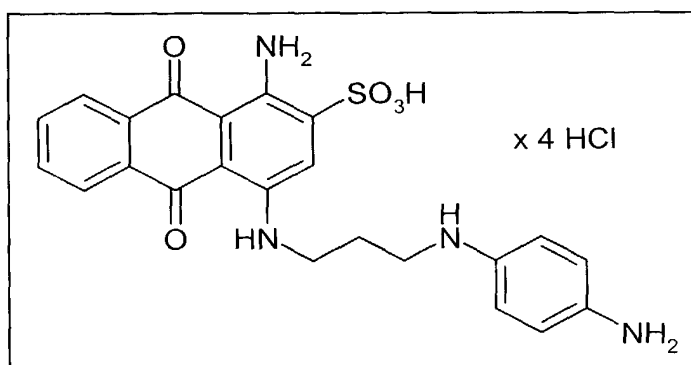
40

PCT/EP00/06159

propyl)-amino)-anthracene-9,10-dione in 340 ml of ethanol was hydrogenated at 25°C (1013 mbar) in the presence of 0.2 g Pd (5%) on carbon. After the uptake of hydrogen has stopped, the solution was acidified with dilute hydrochloric acid, filtered off from the catalyst and concentrated to dryness. A red solid with a melting point above 170°C (decomp.) was obtained.

1.2. 1-Amino-4-((3-((4aminophenyl)-amino)-propyl)-amino)-anthracene-9,10-dione-2-sulfonic acid (hybrid dye B)

10



- X derived from a substantive dye (1,4-diaminoanthracene-9,10-dione-2-sulfonic acid)
- 15 Y derived from an oxidation dye precursor of the primary intermediate type (p-phenylenediamine)
- S alkylene group (-CH₂-CH₂-CH₂-)

1st Stage

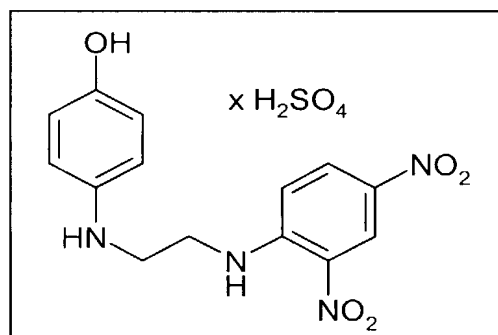
20 A mixture of 100.0 g (0.25 mole) of the Na salt of 1-amino-4-bromoanthraquinone-2-sulfonic acid, 48.3 g (0.25 mole) of N-(p-nitrophenyl)-propylenediamine, 51.8 g (0.37 mole) of potassium carbonate and 0.7 g of Cu powder in 600ml of water were reacted with stirring under nitrogen for 3 h at boiling heat. After cooling, the residue was filtered off

X	derived from a substantive dye (4-amino-2-nitroaniline)
Y	derived from an oxidation dye precursor of the primary intermediate type (p-aminophenol)

S alkylene group (-CH₂-CH₂-)

10.0 g (0.04 mole) of p-(β-aminoethylamino)-phenol sulfate (prepared in accordance with **US 2,618,657**), 8.42 g (42.5 mmoles) of 4-fluoro-3-nitroacetanilide and 6.05 g of sodium hydrogen carbonate were reacted in 40 ml of DMSO with stirring under nitrogen for 3.5 h at a temperature of 65°C. The reaction mixture was then poured onto ice and the deposit was isolated. It was then refluxed for 1 h in 80 ml of dilute hydrochloric acid. The solution was poured onto ice and the deposit 4-((2-((4-amino-2-nitrophenyl)-amino)-ethyl)-amino)-phenol was isolated as a green-brown solid (melting point: 256°C).

1.4. 4-((2-((2,4-dinitrophenyl)-amino)-ethylamino)-phenol sulfate (hybrid dye D)



X derived from a substantive dye (2,4-dinitroaniline)

Y derived from an oxidation dye precursor of the primary intermediate type (p-aminophenol)

S alkylene group (-CH₂-CH₂-)

1st Stage

12.0 g (0.048 mole) of p-(β-aminoethylamino)-phenol sulfate (US

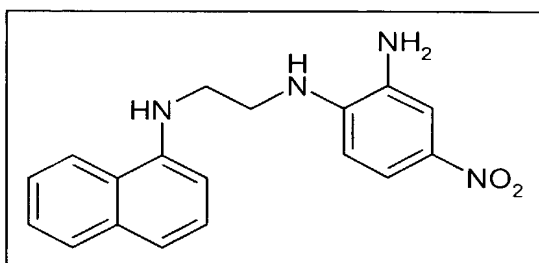
WO 01/02492

43

PCT/EP00/06159

2,618,657), 8.9 g (47.8 mmoles) of 2,4-dinitrofluorobenzene and 6.05 g of potassium carbonate (0.057 mole) were reacted with stirring under nitrogen in 150 ml of ethanol for 2.5 h at boiling heat. The solution was then cooled and filtered off from the salts. The filtrate was adjusted to pH 2 with dilute
 5 sulfuric acid, the deposit was isolated and recrystallized from ethanol/water. The product was obtained in the form of brown crystals with a melting point of 238°C (decomp.).

1.5 (2-((2-amino-4-nitrophenyl)-amino)-ethyl)-naphthylamine (hybrid dye E)
 10



X derived from a substantive dye (2-amino-4-nitroaniline)

15 Y derived from an oxidation dye precursor of the secondary intermediate type (1-naphthylamine)

S alkylene group (-CH₂-CH₂-).

1st Stage

20 10.0 g (38.6 mmoles) of N-(1-naphthyl)-ethylenediamine dihydrochloride were dissolved in a little water and neutralized with dilute sodium hydroxide solution. After the addition of 120 ml of ethanol and 6.4 g of potassium carbonate (46.3 mmoles), 7.2 g (38.7 mmoles) of 2,4-dinitrofluorobenzene were added dropwise. After refluxing for 1 hour, the
 25 whole was cooled to room temperature and the deposit was filtered off under suction and washed with water/ethanol. The intermediate product

A mixture of 8.0 g (47.8 mmol) of 3,5-dimethoxybenzylamine, 7.47 g of 4-fluoro-3-nitroaniline (47.8 mmol) and 7.93 g of potassium

A warm solution of 5.0 g (21 mmoles) of $\text{Na}_2\text{S} \times 9\text{H}_2\text{O}$ and 1.34 g of sulfur in 10 ml of ethanol was added to a solution of 7.2 g (20.9 mmoles) of 1-(2,4-dinitrophenyl)-5,6-dimethoxyindoline and 0.8 g of NaOH in 200 ml of ethanol/134 ml of water. After refluxing for 3 h, the solution was hot-
 5 filtered. Half the filtrate was concentrated and adjusted to pH 7 with concentrated hydrochloric acid. The deposit precipitating on cooling was isolated and washed with water/ethanol. The product was obtained as an isomer mixture (reduction preferably at the ortho as opposed to the para position in a ratio of ca. 4:1, as determined by NMR spectroscopy) in the
 10 form of brown crystals with a melting range of about 115 to 130°C.

2. Coloring

A cream base with the following composition was first prepared [all quantities in g unless otherwise indicated]:

15

tallow fatty alcohol	17.0
Lorol® techn. ¹	4.0
Texapon® N 28 ²	40.0
Dehyton® K ³	25.0
20 Eumulgin® B2 ⁴	1.5
distilled water	12.5

- ¹ C₁₂₋₁₈ fatty alcohol (HENKEL)
- ² sodium lauryl ether sulfate (ca. 28% active substance; CTFA name:
 25 Sodium Laureth Sulfate) (HENKEL)
- ³ fatty acid amide derivative of betaine structure with the formula
 R-CONH(CH₂)₃N⁺(CH₃)₂CH₂COO⁻ (ca. 30% active substance; CTFA
 name: Cocoamidopropyl Betaine) (HENKEL)
- ⁴ cetylstearyl alcohol containing ca. 20 moles EO (CTFA name:
 30 Cetareth-20) (HENKEL)

The following hair coloring cream emulsion was then prepared on the basis of this cream:

5	cream base	50.0
	primary intermediate	7.5 mmoles
	secondary intermediate	7.5 mmoles
	Na ₂ SO ₃ (inhibitor)	1.0
	(NH ₄) ₂ SO ₄	1.0
10	conc. ammonia solution to pH 10	
	water to 100	

The constituents were mixed together in the above order. After addition of the oxidation dye precursors and the inhibitor, the emulsion was first adjusted to pH 10 with concentrated ammonia solution and then made up to 100 g with water.

The color was oxidatively developed with 3% hydrogen peroxide solution as the oxidizing solution. To this end, 50 g of hydrogen peroxide solution (3%) were added to and mixed with 100 g of the emulsion.

The coloring cream was applied to ca. 5 cm long tresses of standardized, 90% gray but not specially pretreated human hair and left thereon for 30 minutes at 32°C. On completion of the coloring process, the hair was rinsed, washed with a standard shampoo and then dried.

The following compounds were used as further dyes/dye precursors:

oxidation dye precursors of the primary intermediate type:

E1 p-toluylenediamine

E2 4-aminophenol

E3 2,4,5,6-tetraaminopyrimidine

oxidation dye precursors of the secondary intermediate type:

K1 2,4-diaminophenoxyethanol

WO 01/02492

48

PCT/EP00/06159

K2	1-naphthol
K3	1,3-bis-(2,4-diaminophenoxy)-propane
K4	5-amino-2-methylphenol
K5	4-chlororesorcinol
K6	resorcinol
K7	2-methyl-5-(2'-hydroxyethyl)-aminophenol
K8	3,4-methylenedioxyphenol
K9	2-chloro-6-methyl-3-aminophenol

The results of the coloring tests are set out in the following Table:

Hybrid Dye	Other Dye Precursor	Color of Hair
A	K1	Blue-gray
A	K2	Dark blue
B	K1	Black blue
B	K3	Nordic blue
B	K2	Dark blue
C	K2	Ruby red
C	K3	Dark magenta
C	K6	Flat red
C	K4	Flat red
C	K5	Flat red
C	K7	Gray-ruby
C	K8	Dark ruby
C	K9	Flat red
D	K6	Light yellow
D	K4	Yellow-orange
D	K3	Chamois yellow
D	K5	Pastel yellow
E	E1	Loam-colored

WO 01/02492	49	PCT/EP00/06159
F	E1	Flat red
G	E1	Brown-orange
G	E3	Cream-colored
G	E2	Golden blond
G	-	Ivory colored ^a

^a In this case, coloring was carried out without hydrogen peroxide

WO 01/02492

50

PCT/EP00/06159

CLAIMS

1. A hybrid dye, more particularly for coloring keratin fibers, which corresponds to formula (I):

5 X - S - Y (I)

where

X is a group derived from a substantive dye,

Y is a group derived from

- 10 - an oxidation dye precursor of the secondary or primary intermediate type,
- a derivative of indole or indoline as a precursor of melanin or
- a substantive dye and

S is a direct bond or a spacer group, with the proviso that S is not an
15 alkylene, mono- or polyhydroxyalkylene group where Y is derived from a substantive dye.

2. A hybrid dye as claimed in claim 1, characterized in that Y is a group derived from

- an oxidation dye precursor of the secondary or primary intermediate
20 type or
- a derivative of indole or indoline as a melanin precursor.

3. A composition for coloring keratin fibers, characterized in that it contains a hybrid dye corresponding to formula (I):

25 X - S - Y (I)

where

X is a group derived from a substantive dye,

Y is a group derived from

- 30 - an oxidation dye precursor of the secondary or primary intermediate

type,

- a derivative of indole or indoline as a melanin precursor or
- a substantive dye and

S is a direct bond or a spacer group, with the proviso that S is not an
 5 alkylene, mono- or polyhydroxyalkylene group where Y is derived from a
 substantive dye.

4. A composition as claimed in claim 3, characterized in that it
 additionally contains an oxidation dye precursor of the secondary or
 primary intermediate type.

10 5. A composition as claimed in claim 3 or 4, characterized in that it
 additionally contains a substantive dye.

6. A composition as claimed in any of claims 2 to 5, characterized in
 that it additionally contains a derivative of indole or indoline as the melanin
 precursor.

15 7. A composition as claimed in any of claims 3 to 6, characterized in
 that it contains a surfactant.

8. A composition as claimed in claim 7, characterized in that the
 surfactant is an anionic surfactant.

9. A composition as claimed in any of claims 3 to 8, characterized in
 20 that it contains a cationic polymer or an amphopolymer.

10. A composition as claimed in any of claims 3 to 9, characterized in
 that it contains an anionic or nonionic polymer.

11. The use of the hybrid dye of formula (I) claimed in claim 1 or 2 for
 coloring keratin fibers, more particularly human hair.

25 12. The use of the hybrid dye of formula (I) claimed in claim 1 or 2 for
 coloring human skin.

"Express Mail" mailing label number EV 105943582 US

Date of Deposit _____

PTO/SB/01 (6-95)

Approved for use through: 10/31/98 OMB 0651-0032

Type a plus sign (+) inside this box → ☐

Patent and Trademark Office; U. S. DEPARTMENT OF COMMERCE

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION <input type="checkbox"/> Declaration Submitted with Initial Filing OR <input checked="" type="checkbox"/> Declaration Submitted after Initial Filing	U. S. Department of Commerce Patent and Trademark Office	Attorney Docket Number	H 3170 PCT/US
		First Named Inventor	Hollenberg, Detlef
	COMPLETE IF KNOWN		
	Application Number	10/031,740	
	Filing Date		
	Group Art Unit		
	Examiner Name		

As a below named inventor, I hereby declare that.

My residence, post office address, and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

NOVEL DYES AND COLORANTS

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 07/01/2000 as United States Application Number or PCT International

Application Number PCT/EP00/06159 and was amended on (MM/DD/YYYY) _____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56

I hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority	Certified Copy Attached?	
			Not Claimed	YES	NO
199 30 927.2	Germany	07/06/1999	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

Burden Hour Statement. This form is estimated to take .4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington DC 20231.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro



(43) Internationales Veröffentlichungsdatum
11. Januar 2001 (11.01.2001)

PCT

(10) Internationale Veröffentlichungsnummer
WO 01/02492 A1

(51) Internationale Patentklassifikation⁷: C09B 51/00,
1/28, 1/30, 69/00, A61K 7/13

Urdenbacher Allee 57, D-40593 Düsseldorf (DE).
WOLFRAM, Leszek, J. [US/US]; 666 Westover Road,
Stamford, CT 06902 (US).

(21) Internationales Aktenzeichen: PCT/EP00/06159

(22) Internationales Anmeldedatum:
1. Juli 2000 (01.07.2000)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
199 30 927.2 6. Juli 1999 (06.07.1999) DE

(71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von
US): HENKEL KOMMANDITGESELLSCHAFT AUF
AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düssel-
dorf (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder (nur für US): HOLLENBERG,
Detlef [DE/DE]; Fliederweg 31, D-40699 Erkrath (DE).
HÖFFKES, Horst [US/US]; Carlo-Schmid-Strasse 113,
D-40595 Düsseldorf (US). FOITZIK, Joachim-Kurt
[DE/DE]; Auf der Letteilung 8, D-64342 Seeheim-Jugen-
heim (DE). ROSE, David [GB/DE]; Am Eichelkamp 223,
D-40723 Hilden (DE). NAUMANN, Frank [DE/DE];

(81) Bestimmungsstaaten (national): AE, AL, AM, AU, AZ,
BA, BB, BG, BR, BY, CA, CN, CR, CU, CZ, DM, EE,
GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LV, MA, MD, MG, MK,
MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, SL,
TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Bestimmungsstaaten (regional): ARIPO-Patent (GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eura-
sisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI,
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI-Patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE,
SN, TD, TG).

Veröffentlicht:

- Mit internationalem Recherchenbericht
- Vor Ablauf der für Änderungen der Ansprüche geltenden
Frist; Veröffentlichung wird wiederholt, falls Änderungen
entfallen

Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

(54) Title: NOVEL DYES AND COLORANTS

(54) Bezeichnung: NEUE FARBSTOFFE UND FÄRBEMITTEL

(57) Abstract: The invention relates to hybrid dyes of structure (I), X - S - Y, wherein X represents a group that is derived from a direct-dyeing dye, Y represents a group that is derived from a coupler or developer-type oxidation dye pre-product, a derivative of indol or indoline as a precursor of the melanin or a direct-dyeing dye, and S represents a direct bond or a spacer group, on the condition that S does not represent an alkylene, mono- or poly-hydroxyalkylene group if Y is derived from a direct-dyeing dye. Said hybrid dyes are excellently suited to dyeing fibers containing keratin, especially human hair. The use of colorants with these dyes avoids or significantly minimizes a number of problems that occur with the use of complex dye mixtures.

(57) Zusammenfassung: Hybridfarbstoffe der Struktur (I), X - S - Y, in der X steht für eine Gruppe, die abgeleitet ist von einem direktziehenden Farbstoff, Y steht für eine Gruppe, die abgeleitet ist von einem Oxidationsfarbstoffvorprodukt vom Kuppler- oder Entwicklertyp, einem Derivat des Indols oder Indolins als Vorläufer des Melanins oder einem direktziehenden Farbstoff, und S steht für eine direkte Bindung oder eine Spacer-Gruppe mit der Maßgabe, daß S nicht für eine Alkyl-, Mono- oder Poly-hydroxyalkylen-gruppe steht, wenn Y von einem direktziehenden Farbstoff abgeleitet ist, eignen sich hervorragend zum Färben keratinischer Fasern, insbesondere menschlicher Haare. Durch Verwendung von Färbemitteln mit diesen Farbstoffen lassen sich eine Reihe von Problemen, die bei Verwendung komplexer Farbstoffmischungen auftreten, umgehen oder deutlich minimieren.

WO 01/02492 A1

1110337441 00000000

Type a plus sign (+) inside this box → ☐

H 3170 PCT/US

2-00

DEX

3-00

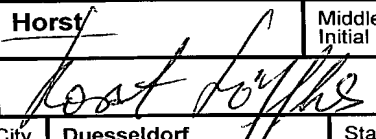
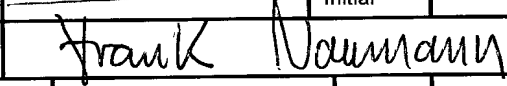
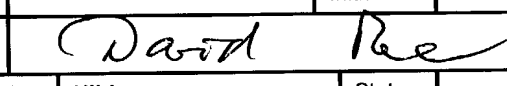
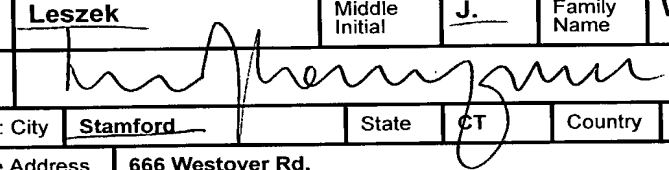
DEX

4-00

DEX

5-00

CT

DECLARATION										ADDITIONAL INVENTOR(S) Supplemental Sheet											
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor											
Given Name		Horst			Middle Initial				Family Name		Hoeffkes			Suffix e.g. Jr.							
Inventor's Signature										Date		20.2.02									
Residence: City		Duesseldorf			State				Country		Germany			Citizenship		Germany					
Post Office Address		Carlo-Schmid-Str. 113																			
Post Office Address																					
City		40595 Duesseldorf			State				Zip				Country		Germany			Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor											
Given Name		Frank			Middle Initial				Family Name		Naumann			Suffix e.g. Jr.							
Inventor's Signature										Date		05.04.02									
Residence: City		Duesseldorf			State				Country		Germany			Citizenship		Germany					
Post Office Address		Urdenbacher Allee 57																			
Post Office Address																					
City		40593 Duesseldorf			State				Zip				Country		Germany			Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor											
Given Name		David			Middle Initial				Family Name		Rose			Suffix e.g. Jr.							
Inventor's Signature										Date		11/04/02									
Residence: City		Hilden			State				Country		Germany			Citizenship		Great Britain					
Post Office Address		Am Eichelkamp 223																			
Post Office Address																					
City		40723 Hilden			State				Zip				Country		Germany			Applicant Authority			
Name of Additional Joint Inventor, if any:										<input type="checkbox"/> A petition has been filed for this unsigned inventor											
Given Name		Leszek			Middle Initial		J.		Family Name		Wolfram			Suffix e.g. Jr.							
Inventor's Signature										Date		4/26/02									
Residence: City		Stamford			State		CT		Country		US			Citizenship		US					
Post Office Address		666 Westover Rd.																			
Post Office Address																					
City		Stamford			State		CT		Zip		06902		Country		US			Applicant Authority			
<input checked="" type="checkbox"/>		Additional inventors are being named on supplemental sheet(s) attached hereto																			

Type a plus sign (+) inside this box → ☐

DECLARATION

ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any:

☐

A petition has been filed for this unsigned inventor

Given Name Joachim-Kurt Middle Initial Family Name Foitzik Suffix e.g. Jr.

Inventor's Signature Joachim Kurt Foitzik Date 01.02.2002

Residence: City Seeheim-Jugenheim State Country Germany Citizenship Germany

Post Office Address Auf der Letteilung 8

Post Office Address

City 64342 Seeheim-Jugenheim State Zip Country Germany Applicant Authority

Name of Additional Joint Inventor, if any:

☐

A petition has been filed for this unsigned inventor

Given Name Middle Initial Family Name Suffix e.g. Jr.

Inventor's Signature Date

Residence: City State Country Citizenship

Post Office Address

Post Office Address

City State Zip Country Applicant Authority

Name of Additional Joint Inventor, if any:

☐

A petition has been filed for this unsigned inventor

Given Name Middle Initial Family Name Suffix e.g. Jr.

Inventor's Signature Date

Residence: City State Country Citizenship

Post Office Address

Post Office Address

City State Zip Country Applicant Authority

Name of Additional Joint Inventor, if any:

☐

A petition has been filed for this unsigned inventor

Given Name Middle Initial Family Name Suffix e.g. Jr.

Inventor's Signature Date

Residence: City State Country Citizenship

Post Office Address

Post Office Address

City State Zip Country Applicant Authority

☐ Additional inventors are being named on supplemental sheet(s) attached hereto

Type a plus sign (+) inside this box → ☐

H 3170 PCT/US

DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112 1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/06159	07/01/2000	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name Customer Number or label

☒ List Attorney(s) and/or agent(s) name and registration number below

Name	Registration Number	Name	Registration Number
Wayne C. Jaeschke	21,062		
Glenn E. J. Murphy	33,539		
Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to: ☒ Customer Number ☐ or label **00423** OR ☐ Fill in correspondence address below

Name	Kimberly R. Hild		
Address	Henkel Corporation		
Address	2500 Renaissance Blvd, Suite 200		
City	Gulph Mills	State	PA
Zip	19406		
Country	USA	Telephone	610-278-4964
Fax	610-278-6548		

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name	<u>Detlef</u>	Middle Initial		Family Name	<u>Hollenberg</u>	Suffix e.g. Jr.	
Inventor's Signature	<u>Detlef Hollenberg</u>				Date	<u>14.03.02</u>	
Residence: City	<u>Erkrath</u>	State		Country	<u>Germany</u>	Citizenship	<u>Germany</u>
Post Office Address	<u>Fliederweg 31</u>						
Post Office Address							
City	<u>40699 Erkrath</u>	State		Zip		Country	<u>Germany</u>
Applicant Authority							

☒ Additional inventors are being named on supplemental sheet(s) attached hereto